

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization
International Bureau



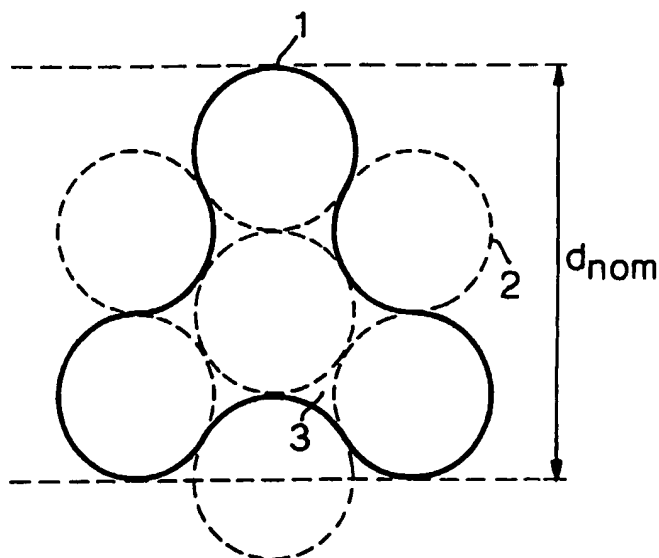
(43) International Publication Date
20 February 2003 (20.02.2003)

PCT

(10) International Publication Number
WO 03/013725 A1

- (51) International Patent Classification⁷: **B01J 35/02**, C10G 47/12 (74) Agent: **SHELL INTERNATIONAL B.V.**; Intellectual Property Services, P.O. Box 384, NL-2501 CJ The Hague (NL).
- (21) International Application Number: PCT/EP02/08540 (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NO, NZ, OM, PH, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZM, ZW.
- (22) International Filing Date: 30 July 2002 (30.07.2002)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data: 01202922.9 1 August 2001 (01.08.2001) EP (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (71) Applicant (*for all designated States except US*): **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ, B.V.** [NL/NL]; Carel Van Bylandtlaan 30, 2596 HR The Hague, (NL).
- (72) Inventors; and (75) Inventors/Applicants (*for US only*): **VAN HASSELT, Bastiaan, Willem** [NL/NL]; Badhuisweg 3, NL-1031 CM Amsterdam (NL). **MESTERS, Carolus, MATTHIAS, Anna Maria** [NL/NL]; Badhuisweg 3,, 1031 CM_Ams-terdam, (NL).
- Published:
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: SHAPED TRILOBAL PARTICLES



(57) Abstract: An elongate, shaped particle comprising three protrusions each extending from and attached to a central position aligned along the central longitudinal axis of the particle, the cross-section of the particle occupying the area encompassed by the outer edges of six outer circles around a central circle minus the area occupied by three alternating outer circles, wherein each of the six outer circles is touching two neighbouring outer circles and wherein three alternating outer circles are equidistant to the central circle, have the same diameter, and may be attached to the central circle.

WO 03/013725 A1

SHAPED TRILOBAL PARTICLES

FIELD OF THE INVENTION

The present invention relates to formed particles having a specific shape which particles may be employed in a wide variety of duties, catalytic or non-catalytic. They can be suitably applied to prevent or substantially reduce fouling of catalyst beds exposed to charges containing fouling material, thereby reducing increases in pressure drop. They can also be applied in hydroprocessing, e.g. in hydrodesulphurisation and hydrocracking, e.g. to produce middle distillates from paraffinic material obtained via a Fischer-Tropsch process.

BACKGROUND OF THE INVENTION

In the past a tremendous amount of work has been devoted to the development of particles, in particular catalytically active particles, for many different processes. There has also been a considerable effort to try to understand the advantages and sometimes disadvantages of effects of shape when deviating from conventional shapes such as pellets, rods, spheres and cylinders for use in catalytic as well as non-catalytic duties.

Examples of further well-known shapes are rings, cloverleaves, dumbbells and C-shaped particles. Considerable efforts have been devoted to the so-called "polylobal"-shaped particles. Many commercial catalysts are available in TL (Trilobe) or QL (Quadrulobe) form. They serve as alternatives to the conventional cylindrical shape and often provide advantages because of

their increased surface-to-volume ratio which enables the exposure of more catalytic sites thus providing more active catalysts.

5 An example of a study directed to effects of different shapes on catalytic performance can be found in the article by I. Naka and A. de Bruijn (J. Japan Petrol. Inst., Vol. 23, No. 4, 1980, pages 268-273), entitled "Hydrodesulphurisation Activity of Catalysts with Non-Cylindrical Shape". In this article experiments have been described in which non-cylindrical extrudates with cross-sections of symmetrical quadrulobes, asymmetrical quadrulobes and trilobes as well as cylindrical extrudates with nominal diameters of 1/32, 1/16 and 1/12 inch were tested in a small bench scale unit on their hydrodesulphurisation activity (12 %wt MoO₃ and 4 %wt CoO on gamma alumina). It is concluded in this article that the HDS activity is strongly correlated with the geometrical volume-to-surface ratio of the catalyst particles but independent of catalyst shape.

20 In EP-A-220933, published in 1987, it is described that the shape of quadrulobe-type catalysts is important, in particular with respect to a phenomenon known as pressure drop. From the experimental evidence provided it appears that asymmetric quadrulobes suffer less from pressure drop than the closely related symmetrical quadrulobes. The asymmetrically shaped particles are described in EP-A-220933 by way of each pair of protrusions being separated by a channel which is narrower than the protrusions to prevent entry thereinto by the protrusions of an adjacent particle. It is taught in EP-A-220933 that the shape of the particles prevents them from "packing" in a bed causing the overall bulk density of the catalyst bed to be low.

Since many of the findings in the art are conflicting and pressure drop problems continue to be in existence, especially when surface-to-volume ratios are increased by reducing particle size, there is still considerable room to search for alternative shapes of (optionally catalytically active) particles which would diminish or even prevent such problems. It has now surprisingly been found that specifically shaped particles of the general "trilobal" shape offer unexpected and sizeable advantages compared with conventional "trilobal" particles, both in catalytic and non-catalytic duty.

DETAILED DESCRIPTION OF THE INVENTION

The present invention therefore relates to an elongate, shaped particle comprising three protrusions each extending from and attached to a central position aligned along the central longitudinal axis of the particle, the cross-section of the particle occupying the area encompassed by the outer edges of six outer circles around a central circle minus the area occupied by three alternating outer circles, wherein each of the six outer circles is touching two neighbouring outer circles and wherein three alternating outer circles are equidistant to the central circle, have the same diameter, and may be attached to the central circle.

It has been found that the particles according to the present invention, having a larger surface-to-volume ratio than corresponding conventional "trilobal" particles of similar size, suffer substantially less from pressure drop than such corresponding conventional "trilobal" particles. Moreover, the shape of the particles according to the present invention allows a certain degree of "packing" which according to the

teaching of EP-A-220993 would be detrimental with respect to pressure drop.

It has also been found that particles having a shape in accordance with the present invention perform
5 exceptionally well when used as a grading material to capture fouling, thereby guarding a fixed-bed reactor against pressure drop increase. It is also believed that catalysts based on particles in a shape according to the present invention are capable of improved performance
10 when used in mass transfer or diffusion limited reactions in fixed-bed reactors, for instance as hydrocracking catalysts in the hydrocracking of paraffinic materials produced from synthesis gas via the Fischer-Tropsch process.

15 The particles according to the invention are elongate and have three protrusions, each running along the entire length of the particle. The cross-section of the particles can be described as the area encompassed by the outer edges of six circles around a central circle minus
20 the area occupied by three alternating outer circles.

Each of the six outer circles is touching two neighbouring outer circles and does not overlap with the two neighbouring outer circles. The six outer circles can be seen as two sets of alternating outer circles, i.e.
25 the three alternating outer circles that are within the cross-sectional area and the remaining three alternating outer circles. The three alternating circles are equidistant to the central circle, have the same diameter, and may be attached to the central circle. The
30 distance to the central circle and the diameter of the circles may be different for both sets of alternating outer circles.

Preferred particles according to the present invention have a cross-section in which three alternating circles have a diameter in the range between 0.74 and 1.3 times the diameter of the central circle. Preferably, all six outer circles have a diameter in this range.

More preferred particles according to the present invention are those having a cross-section in which three alternating circles have the same diameter as the central circle. Preferably, all six outer circles have the same diameter as the central circle.

Most preference is given to particles having a cross-section in which three alternating circles are touching the central circle. Preferably, all six outer circles are touching the central circle.

In Figure 1 a cross-sectional view of the most preferred particles according to the invention has been depicted. The cross-sectional area of the particle of Figure 1 is the area within the solid line 1. It will be clear from this Figure (depicting the cross-section of the preferred particles) that in the concept of six outer circles of even size aligned around a central circle of the same size, each outer circle touches its two neighbour outer circles and the central circle whilst subtraction of three alternating outer circles (dotted line 2) provides the remaining cross-sectional area, built up from four circles (the central circle and the three remaining alternating outer circles) together with the six areas (3) formed by the inclusions of the central circle and six times two adjacent outer circles. The nominal diameter for the preferred particles is indicated as d_{nom} in Figure 1.

The cross-sectional circumference of the particles according to the present invention is such that it forms

a smooth line, which can also be expressed as the function describing the cross-sectional circumference being continuously differentiable.

5 It will be clear that minor deviations from the shape as defined are considered to be within the scope of the present invention. It is known to those skilled in the art to manufacture die-plates which tolerances can be expected in practice when producing such die-plates.

10 It is possible to produce particles according to the present invention which also contain one or more holes along the length of the particles. For instance, the particles can contain one or more holes in the area formed by the central cylinder (the central circle in the cross-section given in Figure 1) and/or one or more holes
15 in one or more of the alternating cylinders (the alternating outer circles in the cross-section given in Figure 1). The presence of one or a number of holes causes an increase of the surface-to-volume ratio which in principle allows exposure of more catalytic sites and,
20 in any case, more exposure to incoming charges which may work advantageously from a catalytic and/or fouling rejection point of view. Since it becomes increasingly difficult to produce hollow particles as their size becomes smaller, it is preferred to use massive particles
25 (still having their micropores) when smaller sizes are desired for certain purposes.

It has been found that the voidage of the particles according to the present invention is well above 50% (voidance being defined as the volume fraction of the
30 open space present in a bed of particles outside the particles present, i.e. the volume of the pores inside the particles are not included in the voidage). The particles used in the experiment to be described

hereinafter had a voidage of typically 58% which is substantially above that of the comparative "trilobal" particle, the voidage of which amounted to just over 43%.

5 The particles according to the present invention can be described as having a length/diameter ratio (L/D) of at least 2. The diameter of the particles is defined as the distance between the tangent line that touches two protrusions and a line parallel to this tangent line, that touches the third protrusion. It is indicated as d
10 nom in Figure 1. Preferably, the particles according to the present invention have a L/D in the range between 2 and 5. For example, the particles used in the experiment to be described hereinafter had a L/D of about 2.5.

15 The length of the particles in accordance with the present invention is suitably in the range between 1 and 25 mm, preferably in the range between 3 and 20 mm, depending on the type of application envisaged. For use in fouling control and in hydrodesulphurisation particles can conveniently be used which have a diameter in the
20 range between 2 and 5 mm.

The shaped particles can be formed of any suitable material provided it is capable of being processed through die-plates giving them their intended shape. Preference is given to porous materials which can be used
25 in catalytic as well as in non-catalytic applications. Examples of suitable materials are inorganic refractory oxides such as alumina, silica, silica-alumina, magnesia, titania, zirconia and mixtures of two or more of such materials. The choice of the material will normally
30 depend on the envisaged application. It is also possible to use synthetic or natural zeolites, or mixtures thereof, optionally together with one or more of the refractory oxides referred to hereinabove, as the

material(s) to be used to form the shaped particles according to the present invention. Good results can be obtained with (catalytically active) particles based on alumina, in particular with gamma-alumina, and various forms of silica-alumina, but other materials can also be applied satisfactorily.

In the event that the particles according to the invention are to be used in catalytic processes, the appropriate amount(s) of catalytically active metal(s) and/or metal compound(s) will have to be present on the particles, which then serve as catalyst carrier (in addition to their capacity to abate fouling as the case may be). Those skilled in the art know which metal(s) and/or metal compound(s) to apply for specific applications and also to which extent and how to incorporate the chosen moieties on the particles envisaged.

When, for instance, hydrodesulphurisation of hydrocarbonaceous feedstocks is envisaged, the shaped particles according to the present invention will normally contain one or more metal(s) of Group VI and/or one or more non-noble metal(s) of Group VIII of the Periodic Table of the Elements which are conveniently present as oxides and/or as sulphides. When the expression "hydrodesulphurisation" is used throughout this specification it also includes hydrodenitrogenation and hydrogenation as these hydrotreating processes normally take place at the same time.

Hydrodesulphurisation conditions normally comprise a temperature in the range between 150 and 400 degrees centigrade, a hydrogen partial pressure up to 80 bar and a LHSV in the range between 1 and 20 Nl feed/l

catalyst/hr. The H_2 /hydrocarbon feed ratio is suitably in the range from 100 to 2000 Nl/l.

The particles according to the present invention can be used advantageously in guard bed duty. Guard beds are normally applied to protect other catalytic beds downstream of the guard bed against unwanted influences caused by the feedstream to be processed over such catalytic beds.

Fouling is one of the most encountered problems when processing feedstocks through one or more catalytic beds. The fouling observed can be caused by impurities in the feedstock which were either present already or which may have been formed during the process. Examples of impurities present in the feedstock to be treated are, for instance, metal-containing particles and/or clay or salt particles which had not or had only been removed incompletely prior to processing over the appropriate catalytic bed(s). Examples of impurities formed during processing are, for instance, fragments of catalytic active particles which were removed from the catalytic bed(s) which in recycle operation are passed through such catalytic bed(s) or coke particles formed during exposure of the feedstock to (severe) process conditions.

Guard beds are normally placed upstream of the bed(s) used in the catalytic process. One or more guard beds can be used to absorb the impurities, thereby delaying the occurrence of pressure drop which allows a longer on stream time of the process envisaged. It is also possible to provide part or all of the particles forming the guard bed with catalytically active materials, thereby combining guard and reaction duty. It is also possible to incorporate catalytically active material of a different nature than that used in the process as envisaged in the

particles of the guard bed. For instance, materials active in hydrotreating may be present in and/or on the particles forming the guard bed(s) having the duty to protect one or more catalyst beds used in hydrocracking and placed downstream of the guard bed. The type and amount of catalytically active materials present in such guard beds are well known in the art and those skilled in the art know how to employ them.

Specific applications for the particles according to the present invention are as grading layers to protect fixed-bed reactors prone to heavy (feedstock originating) fouling which may occur in hydroconversion, in particular in hydrodemetallisation processes, long residue hydro-desulphurisation processes and in the processing of thermally cracked material and to protect fixed-bed reactors suffering from fines deposition deep in the catalytic beds, for instance in units processing synthetic crudes.

It has been found that the beds containing particles according to the invention have - in a random packing - a much higher voidage than beds containing the corresponding conventional trilobes when packed using the well known "sock loading" technique. The voidage obtained when using the conventional trilobal shape amounts to about 45% whereas use of the particles according to the present invention produces a voidage of at least 55% which makes such particles attractive for low pressure drop applications, for instance under conditions of countercurrent gas-liquid flow.

The particles according to the present invention can also be suitably applied in a process for the production of middle distillates from synthesis gas in which heavy paraffinic material produced from carbon monoxide and

hydrogen is subjected to a hydrocracking process to produce middle distillates in the presence of a catalyst containing particles according to the present invention which also contain one or more metals(s) and/or metal compound(s) possessing the desired catalytic activity.

The invention will now be illustrated by means of the following non-limiting examples.

EXAMPLE 1

Two model experiments were carried out to monitor the pressure drop under fouling conditions of catalyst particles made up of conventional trilobes (to be referred to hereinafter as TL) and of particles having a shape as shown in Figure 1 (to be referred to hereinafter as STL - "special" trilobes, having a cross-section occupying the area inside seven circles of the same size (the central circle attached by six outer circles of the same size and three alternating outer circles forming part of the cross-section) minus the three remaining outer circles).

The TL particles had a nominal diameter of 2.5 mm, an L/D of about 2.5, and were made of gamma alumina. A randomly packed bed of the TL particles showed a voidage of 43%. They did not contain additional catalytic material. The STL particles had a nominal diameter of 2.8 mm, an L/D of about 2.5, and consisted of material normally used for DN-200 catalysts (commercially available from Criterion Catalyst Company). A randomly packed bed of the STL particles showed a voidage of 58.3%. Both types of particles were obtained by extrusion using an appropriate die plate.

The fouling material used in the two experiments consisted of a mixture of crushed silica and FCC (Fluid

Catalytic Cracking) catalyst. The composition of the fouling material is given in Table 1 below.

TABLE 1

Size (nm)	Fraction (%w/w)	Type of material
1.4-1.7	0.58	silica
1.18-1.4	0.71	silica
0.6-1.18	6.60	silica
0.355-0.6	4.51	silica
0.212-0.355	4.85	silica
0.125-0.212	7.01	silica
< 0.125	75.74	FCC cat.

The experiments were carried out in a single column containing the material to be tested. The column was operated with cocurrent gas (air) and liquid (water) flow at ambient temperature and pressure. Gas and liquid superficial velocities were 100 mm/s and 4 mm/s, respectively. Before each experiment, the packing was properly wetted with clean water.

The experiments started by switching the liquid feed from clean water to a slurry containing 2.94 kg.m³ of the fouling material. This concentration is several orders of magnitude higher than that to be expected under normal operating conditions in order to be able to assess the phenomenon of pressure drop within a relatively short time. It was found that the run time for the TL particles (before a pressure drop of 500 mBar/m was observed) amounted to 1460 seconds whereas the use of STL particles allowed for a run time of no less than 2260 seconds, i.e. a 55% increase compared to the conventionally shaped particles.

EXAMPLE 2

Two experiments were carried out to compare flooding limits occurring when using conventional TL and particles having a shape according to the present invention (in this case, as shown in Figure 1). The particles used in these experiments had the same shapes and compositions as those described in Example 1. A randomly packed bed of the TL particles showed a voidage of 40% and that of STL particles showed a voidage of 55%.

The experiments were carried out in a single column operated countercurrently with n-octane and nitrogen at ambient temperature and 2 bar absolute pressure. Care was taken to ensure uniform gas and liquid distribution. During the experiments, gas flow was increased at a constant liquid flow rate and pressure drop was measured across the column. The flood point is defined as the point where the pressure drop dependence on the gas velocity abruptly changes from an order between one and two to a substantial higher order.

In the experiment carried out with TL, the gas velocity at which flooding started was determined at an absolute pressure of 2 bar and a superficial liquid velocity of 3 mm/s. The STL were tested at the conditions at which the TL showed starting of flooding at 2 bara and a liquid superficial velocity of 3 mm/s. At these conditions, the gas velocity could be increased as much as 3.4 times before the STL showed the onset of flooding. The use of STL, therefore, delayed reaching of flooding conditions substantially.

C L A I M S

1. An elongate, shaped particle comprising three protrusions each extending from and attached to a central position aligned along the central longitudinal axis of the particle, the cross-section of the particle occupying the area encompassed by the outer edges of six outer circles around a central circle minus the area occupied by three alternating outer circles, wherein each of the six outer circles is touching two neighbouring outer circles and wherein three alternating outer circles are equidistant to the central circle, have the same diameter, and may be attached to the central circle.

2. Particle according to claim 1, wherein three alternating outer circles have a diameter in the range between 0.74 and 1.3 times the diameter of the central circle.

5 3. Particle according to claim 2, wherein three alternating outer circles have the same diameter as the central circle.

4. Particle according to any one of the preceding claims, wherein three alternating outer circles are
10 attached to the central circle.

5. Particle according to any one of the preceding claims, having a L/D ratio of at least 2.

6. Particle according to claim 5, having a L/D ratio in the range between 2 and 5.

15 7. Particle according to any one of the preceding claims, having a length in the range between 1 and 25 mm.

8. Particle according to any one of the preceding claims, which has been formed from alumina, silica,

silica-alumina, magnesia, titania, zirconia, a synthetic or natural zeolite or mixtures of two or more of these materials.

5 9. Particle according to any one of the preceding claims, containing one or more metal(s) and/or metal compound(s) having catalytic activity.

10. Particle according to claim 9, containing one or more metal(s) and/or metal compound(s) having hydroprocessing activity, in particular hydrodesulphurisation activity.

10 11. Guard bed containing particles according to one or more of the preceding claims.

12. Process for reducing fouling or the impact of fouling deposition in catalyst beds which comprises contacting a charge containing fouling material with one or more
15 layers of particles according to any one of claims 1-10 or a guard bed according to claim 11.

13. Process for the conversion of an organic charge comprising contacting the charge with a catalyst containing particles according to claim 9 or 10.

20 14. Process according to claim 13, in which the conversion comprises hydrodesulphurisation of a hydrocarbonaceous feedstock.

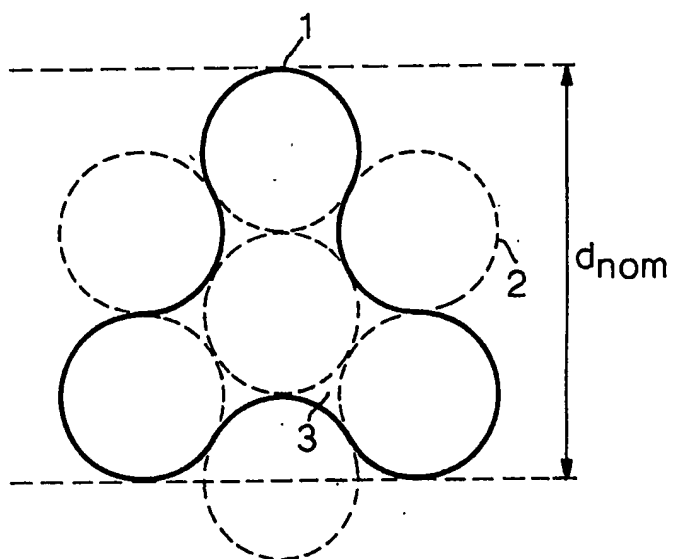
15 15. Process for the production of middle distillates from synthesis gas in which heavy paraffinic material produced from carbon monoxide and hydrogen is subjected to a hydrocracking process to produce middle distillates in the presence of a catalyst containing particles according to any one of claims 1-8 and which contain one or more metal(s) and/or metal compound(s) possessing
25 hydrocracking activity.

16. Process for the conversion of hydrocarbons when carried out under conditions of countercurrent gas-liquid

flow in the presence of particles according to any one of claims 1-10.

1/1

Fig.1.



INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/08540

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J35/02 C10G47/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 B01J C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 446 175 A (AMERICAN CYANAMID CO) 18 August 1976 (1976-08-18) claim 1; figures 8,8A ---	1,7,8
X	US 4 628 001 A (SASAKI HIDEHARU ET AL) 9 December 1986 (1986-12-09) figure 7 ---	1,2
X	US 6 005 121 A (EBNER JERRY R ET AL) 21 December 1999 (1999-12-21) figure 2 ---	1,7,8
A	US 3 764 565 A (JACOBS R ET AL) 9 October 1973 (1973-10-09) claim 1; figures 2B,4B column 2, line 63 -column 3, line 9 --- -/--	1-10

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

T later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

X document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

Y document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

G document member of the same patent family

Date of the actual completion of the international search

22 November 2002

Date of mailing of the international search report

29/11/2002

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax (+31-70) 340-3016

Authorized officer

Veefkind, V

INTERNATIONAL SEARCH REPORT

International Application No

PCT/EP 02/08540

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 464 633 A (KURARAY CO) 8 January 1992 (1992-01-08) -----	
A	EP 0 678 331 A (MONTECATINI TECNOLOGIE SRL) 25 October 1995 (1995-10-25) -----	
A	EP 0 220 993 A (FUJITSU LTD) 6 May 1987 (1987-05-06) cited in the application -----	

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/08540

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
GB 1446175	A	18-08-1976	MY 28380 A	31-12-1980
US 4628001	A	09-12-1986	JP 1719596 C	14-12-1992
			JP 3070011 B	06-11-1991
			JP 61006313 A	13-01-1986
			JP 1721922 C	24-12-1992
			JP 3070012 B	06-11-1991
			JP 61006314 A	13-01-1986
			JP 1033572 B	13-07-1989
			JP 1549242 C	09-03-1990
			JP 61047826 A	08-03-1986
			DE 3576969 D1	10-05-1990
			EP 0168639 A2	22-01-1986
			KR 9203251 B1	25-04-1992
			JP 1823774 C	10-02-1994
			JP 2216222 A	29-08-1990
			JP 5029689 B	06-05-1993
			JP 61006314 T1	13-01-1986
US 6005121	A	21-12-1999	AT 174583 T	15-01-1999
			AU 658217 B2	06-04-1995
			AU 2317892 A	11-02-1993
			BR 9206256 A	10-10-1995
			CA 2110579 A1	21-01-1993
			CN 1068324 A , B	27-01-1993
			CZ 9302822 A3	13-04-1994
			DE 69227906 D1	28-01-1999
			DE 69227906 T2	01-07-1999
			EP 0593646 A1	27-04-1994
			ES 2125902 T3	16-03-1999
			HU 66868 A2	30-01-1995
			IL 102436 A	31-10-1996
			JP 6508850 T	06-10-1994
			KR 9707913 B1	17-05-1997
			MX 9203992 A1	01-08-1993
			NZ 243467 A	27-06-1994
			SK 1994 A3	07-09-1994
			WO 9301155 A1	21-01-1993
			ZA 9205058 A	28-04-1993
US 3764565	A	09-10-1973	US 3674680 A	04-07-1972
EP 0464633	A	08-01-1992	DE 69101032 D1	03-03-1994
			DE 69101032 T2	11-08-1994
			EP 0464633 A1	08-01-1992
			JP 2690408 B2	10-12-1997
			JP 4227069 A	17-08-1992
			US 5371277 A	06-12-1994
EP 0678331	A	25-10-1995	IT 1274033 B	14-07-1997
			AU 689537 B2	02-04-1998
			AU 1626795 A	12-10-1995
			CA 2146184 A1	06-10-1995
			DE 69508637 D1	06-05-1999
			DE 69508637 T2	30-09-1999
			DK 678331 T3	11-10-1999
			EP 0678331 A1	25-10-1995
			ES 2131231 T3	16-07-1999

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP 02/08540

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0678331	A		JP 8038903 A	13-02-1996
			US 5861353 A	19-01-1999
EP 0220993	A	06-05-1987	JP 1775421 C	28-07-1993
			JP 4062663 B	07-10-1992
			JP 62294254 A	21-12-1987
			JP 1912335 C	09-03-1995
			JP 4027546 B	12-05-1992
			JP 62103657 A	14-05-1987
			DE 3687943 D1	15-04-1993
			DE 3687943 T2	17-06-1993
			EP 0220993 A2	06-05-1987
			US 4777103 A	11-10-1988